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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes the results of investigations into the role of potassium salts in modifying flame chemistry and, particularly, the suppression of secondary muzzle-flash. New thermodynamic functions are reported for the potentially significant flame species, KOH, KCl, KO_2, $(KOH)_2$, and $(KCl)_2$. The stabilities of these species is such as to favor cyclic processes with flame propagating radicals such as: (CONT.)

(BLOCK 20. ABSTRACT   Continued)
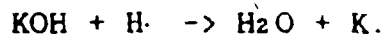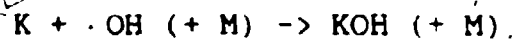
K + ·OH (+ M) -> KOH (+ M).

KOH + H· -> H_2O + K.

Laser spectroscopic observations were made for K atoms in fuel-rich (H-controlled) laboratory flames. Future work is needed to relate such data to the propagation and inhibition of the flames.

MOLECULAR BASIS FOR SECONDARY FLASH SUPPRESSION

FINAL REPORT

J.W. HASTIE
D.W. BONNELL
P.K. SCHENCK

JULY 1, 1986

U.S. ARMY RESEARCH OFFICE

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Molecular Basis for Secondary Flash Suppression

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Molecular Basis for Secondary Flash Suppression

J.W. Hastie, D.W. Bonnell, and P.K. Schenck

I. INTRODUCTION AND OBJECTIVES

An important problem in the design of propellants for guns
is suppression of the muzzle flash and particularly the highly
luminous secondary flash [Cohen and Decker, 1980]. Although it
has been empirically determined through testing of numerous
propellent additives that potassium salts (e.g. one percent
K_2SO_4) are most beneficial in preventing secondary flash
[Carfagno, 1961], the mechanism is still a matter of conjecture,
with recent studies [Heimerl, 1983] suggesting that the mechanism
for potassium salts is homogeneous, involving production of KOH
vapor. It is reasonable to assume that the chemical processes
are similar to those in rocket afterburning and fire suppression,
namely that KOH acts as a radical trap for the flame propagating
radicals via homogeneous cyclic processes such as

$$K + \cdot OH\ (+\ M)\ \rightarrow\ KOH\ (+\ M),$$

$$KOH + H\cdot\ \rightarrow\ H_2O + K$$

net $\quad H + OH \rightarrow H_2O.$
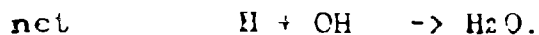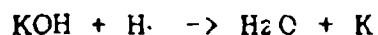
Similar reactions with other species, e.g. KO_2, KCl, $(KOH)_2$, ... are also possible.

To establish such postulated mechanisms, it is first necessary to have reliable thermodynamic data for all potassium containing species present. This includes KOH, for which the available data is extrapolated from lower temperature data using estimated spectroscopic constants; potassium chloride species, as chloride salts are ubiquitous in propellent mixtures; and any oxide species which might be present in the gas phase. Potassium carbonates and nitrates all decompose on vaporization, and recent reliable data are available on the vaporization of K_2SO_4 [Plante. et al, 1983; Lau et al, 1979], where simple vaporization competes with the decomposition reaction.

The basic objectives of this study have been to develop and verify the thermochemistry of species which potentially play a role in the flash suppression mechanism, and to survey the potassium systems for new species to be considered. In addition, rew techniques have been developed for laser spectroscopy and mass spectrometric in situ investigation of flames which are heavily loaded with potassium. These studies were designed to model experimentally the processes occurring downstream of the gun muzzle.

II. KCl VAPORIZATION THERMOCHEMISTRY

Using Transpiration Mass Spectrometry [Bonnell and Hastie, 1977], a technique which permits determining species concentrations and thermochemical data in higher pressure (> 1 atm) environments, new thermodynamic data have been obtained for vapors over KCl and KOH liquids [Hastie, et al, 1983, 1984]. Previous mass spectrometric measurements requiring Knudsen conditions were limited to measurements over solid KCl (MP=1044 K) and solid KOH (MP=673 K). The partial pressure results for KCl show excellent agreement with those based on an extrapolation of the JANAF [1971, 1974] evaluation of solid data.

Supersonic beam analysis indicated a significant variation in the mass spectral ion intensities of $K^+(KCl)$ relative to the $KCl^+(KCl)$ ion as a function of source temperature. As we have noted elsewhere [Hastie and Bonnell, 1983], the final temperature of the supersonic beam depends on orifice size, source temperature and pressure, the local Mach number in the expansion, the gas heat capacity ratio, and molecular collision cross section and effectiveness factors. Where the carrier gas is fixed and the vaporizing species are insignificant to the expansion process, the final gas temperature can be varied by varying the source pressure. Using two different orifice sizes allowed for separating the total pressure from the gas flow rate. Since flow rate varied with pressure and orifice size, it was possible to test for system saturation. The constancy of the

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dimer/monomer ratio, $K_2Cl^+/(K^++KCl)$, versus pressure (and flow rate) showed that the transpiration process sampled from a saturated source environment. This constancy also indicated an absence of excess dimer formation via clustering in the expansion process.

The ratio $K^+/(KCl^+)$ varied strongly with pressure for both orifice sizes, and was identified as arising from a temperature dependent partial cross section for KCl^+ by electron impact. Using either K^+ or $(K^+ + KCl^+)$, we were able to derive partial pressures and thermodynamic parameters for the monomer. Using the excellent agreement of the monomer with the JANAF tables, cross sections for the dimer were derived and partial pressures and thermodynamic data obtained. A slight excess of dimer was noted relative to JANAF above 1200 K, which could indicate temperature dependence in the dimer cross section. The possibility of this effect being due to cluster formation is unlikely. The relative amounts of monomer to dimer are comparable, with the monomer being less than three times the dimer at the melting point.

This work reports the first observation of the $(KCl)_3$ trimer, as the transpiration MS technique allows measurements where vapor pressures are well in excess of that possible in classical Knudsen MS techniques. It was necessary to estimate the cross section of the trimer to obtain partial pressure data. However, based on results with the monomer and dimer, the present results are considered a reliable estimate of the equilibrium

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trimer data. Cluster formation, even if present in the dimer case, is so small that, based on collision frequency arguments, it can clearly be neglected for the trimer.

Polymeric species such as dimers, trimers, etc., are considered important as secondary flash initiation occurs just downstream of the Mach disk, in a region presumed to have been shock-heated after supersonic expansion from the muzzle. The potential for cluster formation in the supersonic expansion is indicated by the following empiricism for the "expansion parameter," which is based on data for gas clustering at high ($< 10^5$) expansion ratios, and near room temperature:

$$45 < P_0 d_0 / (T_c / T_0) < 110 \quad torr\text{-}cm$$

where P_0 is source pressure (in torr), d_0 is the orifice diameter (cm), T_0 is the source temperature, and T_c is the absolute condensation temperature. Values below 45 suggest cluster formation is unlikely, and above 100, that clusters are very likely. For our typical laboratory conditions, maximum expansion parameter values were around 50, hence our concern regarding possible cluster involvement. Also, for typical muzzle throat conditions of 165 atm at 1700 K, and a 9 mm muzzle orifice diameter, the expansion parameter has a value of 5×10^5. Thus, it is likely that polymeric species are present as a result of cluster formation in the expansion even if condensed species (e.g. $K_2 CO_3$ (l) or exhaust particulates) do not have time to form.

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Table I gives selected thermodynamic data from this study for the KCl species present. The reader is referred to Hastie, et al, 1984 for a more complete account of this work.

III. KOH VAPORIZATION THERMOCHEMISTRY

Existing literature data for KOH vaporization is quite uncertain, particularly due to experimental difficulties with sample reactivity. There are widely disparate reports on monomer/dimer ratios, and there is little or no spectroscopic data on the important low frequency vibrational modes needed for third law analysis of partial pressure data. The Transpiration MS sampler, boat carrier, and boat were constructed entirely of platinum for the experimental work with KOH. Less than 10 sq. mm of high grade alumina, used as thermocouple insulation upstream of the sample region, was potentially exposed to the KOH vapor. No evidence of attack or solution of KOH was observed on this insulator.

The latest JANAF evaluation [1974] of the KOH system is based primarily on the third law data for the heat of dimerization from mass spectrometric data of Porter and Schoonmaker [1958] (S&P) and Gusarov and Gorokov [1968] (G&G), and apparently heavily favors the S&P data.

Vapor species from liquid KOH, formed into a molecular beam by supersonic expansion from the transpiration MS inlet system and ionized by electron impact, yield the following positive

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ions: K^+, KOH^+, K_2OH^+, and K_2O^+ in decreasing order of ion intensity. The first two ions are assigned to KOH as the precursor, and the other two to $(KOH)_2$. It is possible that some K^+ arises from the dimer, although the phase data analysis suggests this is a relatively minor process at most. The appearance of K^+ from K atoms, distinguished by the low appearance potential (4.5 eV), was noted in the initial heating stage, along with abnormally high H_2O^+, which suggests the following reaction:

$$2KOH(l) = H_2O + 2K + 1/2O_2 .$$

The presence of platinum in the system apparently drives this reaction forward by adsorbing or dissolving O_2. Another source of atomic K is from K_2O, a likely contaminant in KOH and a likely problem in earlier literature work. By addition of O_2 and H_2O to modify the above equilibrium, we established that the activity of KOH(l) is not affected by the presence of free K in small quantities. G&G convincingly established KOH as the only significant precursor to KOH^+, and electric deflection experiments on the analogous NaOH system supports the above assignments.

Although the K_2O^+ ion signal could conceivably arise from a K_2O gas molecule, present at the much higher temperatures of this study, we could assign most or all of the K_2O^+ ion signal to $(KOH)_2$. The ion intensity ratio K_2O^+/K_2OH^+ was invariant over

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all experimental conditions of temperature and gas flow rate; in addition, when H_2O was added to the carrier gas stream, there was no change in K_2O^+/K_2OH^+. If we assume that as much as ten percent of the K_2O^+ signal comes from K_2O, we derive an average K-O bond energy less than 74 kcal/mole. Comparing this with the corresponding value of 89 kcal/mole in Li_2O, and recognizing that relative stability arguments would predict a lower stability for K_2O, we conclude that ten percent is a conservative upper limit.

To minimize any possible bias, we purified the samples in situ until the excess K^+ was small and used only the invariant signals of KOH^+ and K_2OH^+ as measures of the monomer and dimer respectively.

As in the KCl case, variable system pressure experiments were used to identify any excess dimer arising from clustering. Ion intensities and ratios were found to be essentially constant over the region of linear response of the carrier gas (typically 0.05 - 0.2 atm), and thus the thermochemical measurements were made within this total pressure range. Although a slight variation of ion ratios K^+/KOH^+ and K_2OH^+/KOH^+ were noted, these changes were small and occurred only at gas pressures where downstream scattering was significant, e.g. above ~0.2 atm. Thus, possible cluster formation contributions to the observed dimer ion intensities was less than 15 percent in the worst case. A separate experiment using the small conical orifice and pressures below 0.2 atm eliminated the possibility of cluster formation, yielding similar K^+/KOH^+ and K_2OH^+/KOH^+ ion ratios to the larger

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orifice capillary nozzle experiments. With ~10⁻³ atm of H₂O
vapor added to the nitrogen carrier, this experiment also
established that significant decomposition to produce K had been
eliminated.

Thirty eV cross sections were obtained for the following ion
formation processes, (KOH -> KOH⁺) = 1.1; (KOH -> KOH⁺ + K⁺) ≤ 2.7;
(KOH)₂ -> K₂OH⁺ = 3.6, all relative to N₂ --> N₂⁺ = 1.48 in
πa₀ units.

This experimental work gives vapor pressures for the KOH
monomer within 10 percent of the JANAF evaluation, and in good
agreement with the bulk of the literature. The dimer vapor
pressure results, on the other hand, show that the JANAF
evaluation is quite low, being a factor of 2.5 low at 1000 K, and
with a slope 22 percent lower, indicating that the dimer
contribution at temperatures of importance to the secondary flash
phenomenon would be much lower than we have found to be the case.
Our results are in good agreement with the relative partial
pressures of G&G, including vaporization enthalpy. In addition,
total vaporization studies by Dubois & Millet [1968] and Jackson
and Morgan [1921] both support the higher dimer vapor pressure
and vaporization heat, using the now confirmed monomer pressures
to extract dimer data. Table II gives our recommended values for
the vaporization thermodynamics of the KOH monomer and dimer.

New species observed in this system include the KOH trimer,
and KO₂ in the higher oxygen partial pressure experiments, as
discussed below. The trimer, detected as the ion K₃(OH)₂⁺ only

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at the highest temperatures, was observed over too short a temperature range to determine reliable second law thermodynamic values. The apparent vapor pressure, uncorrected for cross section, was 0.05 that of the dimer at 1000 K. This value is notably similar to the value of 0.04 for the trimer/dimer ratio in the KCl system.

IV. KO_2 STABILITY

In high partial pressures of O_2, ca. 0.1 atm, a new ion was observed, KO_2^+. As the intensity of this ion showed no correlation with intensities of K_2O^+ or K_2OH^+, the dimer $(KOH)_2$ was eliminated as a possible precursor. The most reasonable assignment was KO_2. Using the gas phase reaction

$$2KOH + 1.5\ O_2 = 2KO_2 + H_2O,$$

we obtain $\Delta H_{f,1000}(KO_2) = -73.7\pm13$ kJ/mol and $D_{1000}(K-O_2) = 154\pm13$ kJ/mol for the dissociation energy of KO_2 to yield K and O_2. This dissociation energy is reasonable compared to analogous values for HO_2 and NaO_2 of 197 and 146 ± 21 kJ/mol respectively. Under lean flame conditions, a measurable loss of K atoms should occur due to KO_2 formation, and Kaskan [1965] has noted this effect.

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V. FLAME MEASUREMENTS

1. High Potassium Transport Nebulizer

In order to introduce high levels of potassium into a
laboratory burner, it was necessary to develop a new method for
aspirating potassium salts into the premixed flame gases.
Earlier failures to detect potassium mass spectrometrically in
flames, at the salt loadings of a few 100 ppm possible with
sprayer-type aspirators, led to the need to develop an aspirator
capable of injecting much higher salt concentrations into the
supply gas stream, without clogging lines and valves, and
particularly without fouling the burner. If either condition
occurs, it becomes impossible to calibrate the potassium addition
rate, and thus difficult to quantify detected K^+ with actual
flame concentrations. The entrained water from sprayer-type
aspirators introduces considerable excess H_2O into the flame,
which could perturb the reactions of interest. It also desirable
to be able to turn the potassium feed on and off during a single
experiment to permit difference measurements of potassium
influence on other flame species.

An attractive new design of nebulizer, reported by
Steinberg, is based on a barium titanate piezoelectric
transducer, driven at ultrasonic (ca. one MHz) frequencies by a
variable power RF generator, exciting a column of aqueous
potassium nitrate solution. The result is an aerosol with mean
droplet size estimated to be in the range 1 - 10 microns.

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The physical apparatus consists of a vertically mounted three cm dia. glass cylinder reservoir, 23 cm long, with the transducer assembly bottom mounted in a plexiglas assembly and coupled to the reservoir through a 0.08 mm mylar sheet interface. This allows the transducer to be isolated in a salt-free water region, while coupling efficiently with the salt solution filling approximately half the reservoir. The transducer and power supply were obtained from a commercial ultrasonic system originally manufactured for medical aspiration purposes.

An 1100 SCCM portion of the nitrogen flame diluent gas was introduced to the reservoir three cm above the liquid level to entrain the aerosol. Above the reservoir, a heated (~200 °C) plenum, two cm dia. by 65 cm long evaporated the water from the salt to yield submicron particles. Although provision was made for large agglomerated particles to settle, no evidence for such agglomerations was found. A 35 cm ice water cooled condenser was used to removed excess water vapor. We found this step essential to avoid water condensing later in the system plumbing. A final 30 cm column served to reheat the gas well above ambient to prevent condensation on valve cool surfaces. Downstream of the reservoir, the gas stream flowed at a linear velocity of six to ten cm/s.

On exit from the assembly, the nebulizer gas was mixed with the other flame gases in a small check-valve isolated manifold at the base of the burner. After several hours operation at high transport rates using solutions of up to 1 gm/l KNO_3, it was

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necessary to disassemble the mixing manifold and remove the salt accumulation. The salt accumulation appeared absolutely dry and represented only a minor portion of the total salt nebulized. However, the accumulation did eventually clog the check-valve, and probably represents the largest sized particles. Some form of settling volume is necessary to prevent this accumulation, since clogging the mixing check-valve allows back flow of the combustion mixture, unstable flow metering, and large instantaneous changes in K loading as individual particles work through the valve, as well as providing a trapping point for the much finer average particles. It should be noted that it was never necessary to clean the burner, and that until the check-valve began to clog seriously, the potassium transport could be shut off promptly in the time expected to purge lines of the nebulizer mixture.

An arrangement to permit the reservoir to be refilled to a reference mark from a burette allowed for calibration of the solution transport, and hence permitted absolute calibration of the material loading in the burner. A catch basin below the condenser collected the transported water for comparison with the refill process.

2. Flat Flame Premixed Burner

The burner is a modification of the classical Padley-Sugden burner described by Miller [1979]. This burner is an annular,

shielded, water cooled, laminar system which supports a stiff, isolated $H_2/O_2/N_2$ flame with an essentially flat reaction zone and an unperturbed post-reaction zone over 50 mm long. The inner flame region is supported on 19 stainless steel capillaries .050" OD with .010" walls, giving an inner flame diameter of 0.64 cm. The inner flame is surrounded by two rows of the same capillary (44 tubes), with an open flow area ratio of 2.32 relative to the inner flame.

Three flames were selected and the burner calibrated for this work. The flames chosen follow the Padley-Sugden notation for $H_2/O_2/N_2$ flames, with a leading letter representing the H_2 flow ratio (A = 1.0, B = 1.1, ... O = 3.4, P = 3.5, ... U = 4.0, etc.) relative to O_2, and a number giving the N_2 flow ratio. The flames are given in Table III, along with flame temperatures determined with this burner by a variety of complimentary techniques [Drake, et al, 1979] for the U4 and O2 flames.

3. Optical Absorption Measurements

Laser atomic absorption measurements were made on the combustion apparatus consisting of the burner with a U4 flame and the aspiration system described above. The U4 flame was selected initially from those well characterized earlier [Drake, et al, 1979], because it was expected that the cooler flame would be more sensitive to flame inhibition effects.

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The principle of laser atomic absorption is basically the same as conventional atomic absorption except that the source, usually a hollow cathode lamp, is replaced by a narrow band tunable dye laser. Since the hollow cathode lamp is a spectrally narrow source the absorption coefficient, defined as:

$$a(w) = -1/I(w) * dI(w)/dx$$

is measured at only one value of the frequency w, ie. the line center. The linewidth of the species in the flame is much broader because of Doppler and pressure broadening. The inhomogeneous Doppler broadening is a function of temperature. If only a single wavelength source is used the apparent value of the absorption coefficient will depend upon the local temperature in the flame.

Experimentally, the absorption measurement is a line of sight measurement and the absorption coefficient must be integrated over the absorption path x yielding:

$$I(w) = Io \, exp(-a(w)x)$$

from which the more common form:

$$a(w)x = \ln(Io(w)/I(w))$$

is derived. Note that this is still a function of the frequency w. The number density N is related to the absorption cross section s by:

$$a(w) = Ns(w) = Ns_0 g(w)$$

where $g(w)$ contains the spectral dependence of the cross section s for atomic absorption. To determine the number density, N, we must calculate the value of s_0 from the observed transition strength, or Einstein A coefficient, using:

$$s_0 = (1/4)(g_2/g_1)L_{21}^2 A_{21}$$

where L_{21} is the wavelength, and the g's are the Lanue' g-factors. In addition, we combine the earlier equations for the absorption coefficient to obtain:

$$Ns_0 g(w) = (1/x)\int \ln(I_0(w)/I(w))$$

Experimentally, we measure $I_0(w)/I(w)$ by scanning the narrow band tunable dye laser through the absorption profile of the species in the flame. Integrating both sides of the last equation over frequency yields:

$$N = (1/s_0 x) \int \ln(I_0(w)/I(w))dw$$

It is important to note that this equation means that the number density can be determined by this technique without any knowledge of the flame temperature as long as the wavelength of the laser is known.

The wavelength of the tunable dye laser is controlled by tilting a 0.5mm etalon mounted in the laser cavity. The wavelength of the laser is given by:

$$L = 2nt \cos(\Theta)/m$$

where n is the index of refraction, t the etalon thickness, Θ the tilt angle, and m the order number. For the small angles typical of laser etalon tuning, the frequency w of the laser can be shown to be proportional to the angle squared. Thus the evaluation of the integral over frequency can be simplified if the etalon is scanned appropriately. By scanning the laser two etalon orders through the known wavelength of the absorption line it is possible to exactly calibrate the frequency scan and evaluate the integral to obtain the number density.

To characterize the flame system, the etalon was scanned by a sinusoidal oscillator and the value of I(w) was averaged over successive scans of the etalon with a signal averager. Io(w) was monitored by a separate detector and adjusted later for sensitivity differences with the I(w) detector. A typical scan at 10mm above the burner is shown in Figure 1 over the potassium absorption at 766.5nm. The laser power was about 100mw (average)

and the beam diameter was about 1-2mm. In order to test and characterize the combustion system the integral of Io(w)/I(w) was approximated by simply summing the values of Io/I from each channel of the signal averager to obtain a relative value of the number density of potassium atoms.

Figure 2 shows the relative number density of potassium atoms from 0 to 40 mm above the burner. The number density was determined in sequential scans through the absorption profile at increasing heights. The integral was approximated by summing over the channels which comprise the absorption signal and was zeroed relative to an Io/I sum with no potassium. The general dependence of the concentration is as expected. However, in typical runs the set of scans was repeated in reverse order with different results. This was assumed to be due to contamination of the burner-aspirator system by the high potassium loadings. This was verified by observing the reproducibility of the absorbance measurement at a fixed height. For this reason the error bars on the figure are set at the 25% level. These estimated errors also reflect the power stability of the laser and reproducibility of the wavelength scan.

Although the full implementation of the technique was not attempted due to these problems, the number density of the atomic potassium can be estimated from these scans. The absorbance was typically 0.5 to 1.0, at line center, for a 0.64 cm path length. Combining this with the calculated absorption cross section and the observed half-width of the absorption signal of about 20GHz,

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a density of 2×10^{11} potassium atoms/cc is obtained. The number density of potassium ions, and hence total potassium introduced is 10 to 100 times higher, depending on the local flame temperature. This corresponds to nebulizer operation at 10% of available RF excitation with a KNO_3 solution of 1 gm/l concentration. We estimate that approximately 3 orders of magnitude increase in potassium loading is possible, which should allow for MS detection of the neutral population in an actual flame environment.

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TABLES

TABLE I - KCl(l) Vaporization Thermodynamics

Species	ΔH_v kJ/mol	ΔS_v J/mol.K	$\log_{10}(P)$ atm
KCl	166.9±5	95.2±3	4.972 - 8,717/T
[JANAF	174.9	102.0	5.333 - 9,135/T]
(KCl)$_2$	209.82	127.1±2	6.638 - 10,963/T
[JANAF	193.	110.0	5.755 - 10.092/T]
(KCl)$_3$	145.6±6	36.4±5	1.901 - 7,600/T

TABLE II - KOH(l) Vaporization Thermodynamics

Species	ΔH_v kJ/mol	ΔS_v J/mol.K	$\log_{10}(P)$ atm
KOH	164.0±6	109.2±6	5.703 - 8,566/T
(KOH)$_2$	158.6±7	95.0±7	4.962 - 7,284/T
[JANAF	123.4±17	49.8±13	2.601 - 6,445/T]

TABLE III - Flame Compositions

Flame	H$_2$ / O$_2$ / N$_2$ moles	Peak Flame Temperature K
O2	3.4 / 1 / 2	2485
P3	3.5 / 1 / 3	2237
U4	4.0 / 1 / 4	2046

FIGURE 1

POTASSIUM CONCENTRATION

FIGURE 2